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INTERNAL REPORT PM-M-71-15

ALLOYS OF TITANIUM AND REFRACTORY COMPOUNDS

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ABSTRACT

Thorium oxide and cerium zirconate were alloyed with pure titanium and with two titanium alloys by arc melting. The refractory compounds apparently dissolved during melting and precipitated as dispersed phases on cooling. Although room-temperature and high-temperature (540°C) tensile strengths were improved at the expense of ductility, the refractory particle size and interparticle spacing were larger than recommended for maximum dispersion strengthening. Heat treating increased the size of the refractory particles.

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INTRODUCTION

Our previous work[1] has shown that it is possible to produce arc-melted zirconium alloys containing finely dispersed refractory compounds. Certain oxide refractories dissolve in molten zirconium during arc melting and subsequently precipitate as a dispersed phase on cooling. In this investigation, the possibility of dispersion strengthening titanium by this method was examined. Thorium oxide (ThO_2) and cerium zirconate ($Ce_2O_3 . 2ZrO_2$) additions were made to titanium and to two high-temperature titanium alloys. Attempts to incorporate yttrium oxide (Y_2O_3) by this technique were not successful.

EXPERIMENTAL PROCEDURE

Alloy Preparation

The titanium and alloys in Tables 1 and 2 as well as Ti-1.5% thoria and Ti-2.5% yttria were prepared with titanium sponge (containing 550 ppm oxygen), 99.99% pure aluminum, 99.7% pure vanadium, and 99.5% pure molybdenum. The refractory compounds - thoria, cerium zirconate and yttria - were in the form of commercially pure powders with particle size of about 4 microns.

Melting and alloying were carried out in a laboratory-size tungsten-arc furnace in an argon atmosphere. The titanium sponge was consolidated by melting into a dense cigar-shaped ingot in which a cavity was drilled to contain the refractory compound. Each charge weighed approximately 65 grams and was remelted at least 4 times to ensure homogeneity. From visual observation during melting, thoria and cerium zirconate appeared to completely dissolve in the molten titanium but the yttria formed a slag-like substance that floated on the top of the ingot and remained on solidification.

Heat-Treating

As indicated in Tables 1 and 2, titanium and titanium alloys were tensile tested in either the arc-melted or the annealed condition. The two annealing heat treatments, shown at the foot of the Tables, are recommended for Ti-6%Al-4%V and Ti-7%Al-4%Mo alloys.

To examine the effect of heat treatment on the dispersed phase in Ti-2.5% thoria and Ti-2.5% cerium zirconate, specimens were heated in vacuum for 24 hours at temperatures ranging from 775°C to 950°C and then were water quenched. Specimens of the Ti-2.5% choria alloy were also held in vacuum at 775°C and 900°C for 14 and 28 days.

Tensile Testing

Tensile tests were conducted in air at room temperature and in a vacuum of 5×10^{-5} torr at 540°C using an Instron universal testing machine. Test specimens had a 1-inch gauge length and a 0.16-inch gauge diameter. All tests were in duplicate.

Electron Microexamination and X-ray Analysis

Specimens for electron microscopy and for X-ray diffraction analysis were first ground on 600-grit silicon-carbide abrasive paper and then polished on 9-micron, 3-micron, and 1/4-micron diamond paste. Finally, the specimens were chemically polished and etched by swabbing for 30 seconds with a solution containing 45 cc nitric acid, 45 cc hydrogen peroxide, and 8 to 10 cc hydrofluoric acid.

For examination by the electron microscope, chromium-shadowed carbon-biodan replicas were taken of polished and etched specimens.

X-ray diffraction analysis of a Ti-2.5% thoria specimen was conducted on a G. E. diffractometer using CuK alpha radiation. A Ti-2.5% cerium zirconate specimen was analyzed using a Si(Li) diode detector and a multichannel analyzer with continuous X-radiation. Combined fluorescence and diffraction patterns were taken using a Siemens' diffractometer at the angles $2\theta = 19.0°$ and $2\theta = 20.0°$.

RESULTS AND DISCUSSION

Tensile Properties

Tables 1 and 2 show that the room-temperature tensile strength of titanium is improved by the addition of thoria and that the high-temperature (540°C) tensile strength is improved by additions of thoria or cerium zirconate. However, the elongation at room temperature is considerably reduced - from 49% to 16% for the alloy containing 2.5% thoria. At 540°C, the addition of refractory compounds has little effect on the elongation of titanium, which is only 13% when unalloyed. This low ductility at 540°C is not uncommon for titanium and titanium alloys and is attributed to strain ageing[2, 3].

When 2.5% thoria is added to a Ti-6%Al-4%V alloy, the tensile strength at 540°C is not improved, and the elongation is reduced from 18% to 10%; the addition of 5% thoria increases the tensile strength from 77.3 ksi to 86.7 ksi with 9% elongation. At room temperature, 5% thoria increases the strength of this alloy from 131.7 ksi to 144.5 ksi and reduces the elongation from 10% to 8%.

Additions of cerium zirconate also increase the tensile strength of the Ti-6%Al-4%V alloy at room temperature and at 540°C but the elongation is reduced to 3% and less.

Table 2 shows also that thoria and cerium zirconate added to a Ti-7%Al-4%Mo alloy again improve the tensile strength at the expense of ductility.

The increase in strength of titanium at 540°C by the addition of thoria is not due to the presence of oxygen resulting from any decomposition of the refractory because oxygen does not have any strengthening effect at this temperature[2]. Also, work by Ripley[4] suggests that titanium does not reduce the thoria in the Ti-2.5% thoria arc-melted alloy. It would

therefore appear that any increase in strength of the Ti-thoria alloys is due to the presence of thoria. It is also reasonable to conclude that the increase in strength of Ti-cerium zirconate alloys is due to the presence of the oxide compound and not to its contained elements.

Microstructure

Structures of arc-melted alloys containing from 1.5% to 5% thoria are shown in the electron micrographs, Figures 1 to 3. A dispersed phase is evident in the structure of the Ti-1.5% thoria alloy shown in Figure 1. In Figure 2, which shows the structure of the Ti-2.5% thoria alloy, the second phase is much coarser. X-ray diffraction analysis of this specimen identified the second phase as thoria (see Table 3). When the thoria content is increased to 5% there is a heavy precipitate at the grain boundaries as well as a finer dispersion throughout the grains as shown in Figure 3; the black spots in this Figure are the result of thoria particles being extracted by the replica.

The varying size and shape of the thoria in the alloys examined is evidence that it dissolves in titanium during arc melting and that the mode of precipitation on cooling depends upon the amount present.

When 2.5% or 5% cerium zirconate is arc melted with titanium there is a dispersion of fine particles, mainly at alpha platelet boundaries, as is shown in Figure 4 (Ti-2.5% cerium zirconate). X-ray analysis shows these particles to be cerium zirconate or cerium oxide - the two diffraction patterns are quite similar (see Table 4). The black spots in the electron micrograph are again the result of the refractory particles being extracted by the replica.

Annealed specimens of the two titanium alloys containing thoria and cerium zirconate exhibit large refractory particles in the microstructures. Figures 5 and 6 show the structure of the Ti-6%Al-4%V alloy with 5% thoria and 5% cerium zirconate, respectively.

Grant[5] has reported that a particle size of less than 0.1 micron and an interparticle spacing of 0.3 micron or less are required for optimum dispersion strengthening. Of the alloys examined, only in Ti-5% thoria does

the particle size and spacing approach the above requirements, but in this alloy there is also massive thoria at the grain boundaries (Figure 3). The Ti-cerium zirconate alloys have fine particles with large spacing (Figure 4), and in all the other alloys both the particle size and spacing are large.

After Ti-2.5% thoria is heat treated for 24 hours at 775°C to 950°C and water quenched, the thoria particles are similar to those in the arc-melted specimens. This can be seen by comparing the structure of the arc-melted alloy in Figure 2 with the structures after heat treating at 775°C and 950°C in Figures 7 and 8, respectively. However, thoria is not completely stable in titanium at these temperatures. After Ti-2.5% thoria alloy specimens are heated at 775°C and 900°C for 14 and 28 days, some of the thoria particles increase in size. The electron micrograph in Figure 9 shows the larger particles in a specimen heated at 900°C for 28 days.

After the Ti-2.5% cerium zirconate alloy has been heat treated for 24 hours at temperatures up to 775°C, there is no visible change in the refractory particles but, after 24 hours at 875°C, some of the particles increase in size and at 950°C they are as large as shown in Figure 10.

CONCLUSIONS

Arc melting of titanium and titanium alloys with additions of thoria or cerium zirconate results in a dispersion of the refractory in the alloy and in increased room-temperature and high-temperature (540°C) tensile strengths, but in reduced ductility. However, the size or spacing of the refractory particles in all the alloys except Ti-5% thoria is larger than required for maximum dispersion strengthening. In the Ti-5% thoria alloy, there is massive thoria at the grain boundaries besides finely dispersed particles. The particle size of the dispersed phase is increased by some heat treatments.

ACKNOWLEDGEMENTS

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TABLE 1

Room Temperature Tensile Properties of Titanium and Titanium Alloys

Nominal Composition wt %	Condition	UTS ksi	0.2% Y.S. ksi	% El on 1 in.
Ti	arc-melted	54.4	33.6	49
Ti-2.5% ThO_2	arc-melted	108.9	86.7	16
Ti-5% ThO_2	arc-melted	78.0	73.9	2
Ti-6%Al-4%V	annealed (a)	131.7	121.3	10
Ti-6%Al-4%V-5% ThO_2	annealed (a)	144.5	132.8	8
Ti-6%Al-4%V-2.5%$Ce_2O_3 . 2ZrO_2$	annealed (a)	156.0	151.2	2

annealed (a) - 830°C for 2 hours, furnace cooled to 595°C then air cooled.

TABLE 2

Tensile Properties of Titanium and Titanium Alloys at 540°C

Nominal Composition wt %	Condition	UTS ksi	0.2% Y.S. ksi	% El on 1 in.
Ti	arc-melted	13.6	12.1	13
Ti-2.5% ThO_2	annealed (a)	24.4	22.8	11
Ti-5% ThO_2	annealed (a)	26.1	24.8	14
Ti-2.5%Ce_2O_3.2ZrO_2	annealed (a)	28.9	21.8	16
Ti-5%Ce_2O_3.2ZrO_2	annealed (a)	35.8	29.4	13
Ti-6%Al-4%V	annealed (a)	77.3	64.8	18
Ti-6Al-4%V-2.5%ThO_2	annealed (a)	78.1	68.1	10
Ti-6%Al-4%V-5%ThO_2	annealed (a)	86.7	74.6	9
Ti-6%Al-4%V-2.5%Ce_2O_3.2ZrO_2	annealed (a)	86.1	75.8	3
Ti-6%Al-4%V-5%Ce_2O_3.2ZrO_2	annealed (a)	89.8	85.8	1.5
Ti-7%Al-4%Mo	annealed (b)	87.0	77.4	16
Ti-7%Al-4%Mo-5%ThO_2	annealed (b)	95.7	74.6	9
Ti-7%Al-4%Mo-2.5%Ce_2O_3.2ZrO_2	annealed (b)	90.6	81.5	3
Ti-7%Al-4%Mo-5%Ce_2O_3.2ZrO_2	annealed (b)	111.4	95.4	2

Annealed (a) - 830°C for 2 hours, furnace-cooled to 595°C then air cooled.
Annealed (b) - 815°C for 1 hour, furnace-cooled to 565°C then air cooled.

TABLE 3

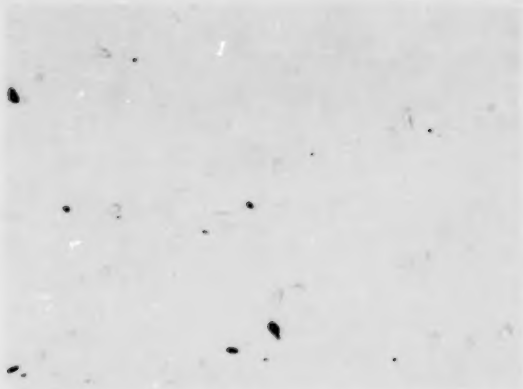
X-Ray Diffraction Analysis of Ti-2.5% Thoria Alloy

2θ	Intensity	Constituent	2θ from ASTM Index
27.65	688/145	ThO_2	27.56
32.05	572/105	ThO_2	31.94
35.10	821/100	Ti	35.06
38.45	4430/95	Ti	38.40
40.28	2813/85	Ti	40.15
45.90	373/50	ThO_2	45.78
53.00	881/50	Ti	53.00
54.25	316/55	ThO_2	54.26

TABLE 4

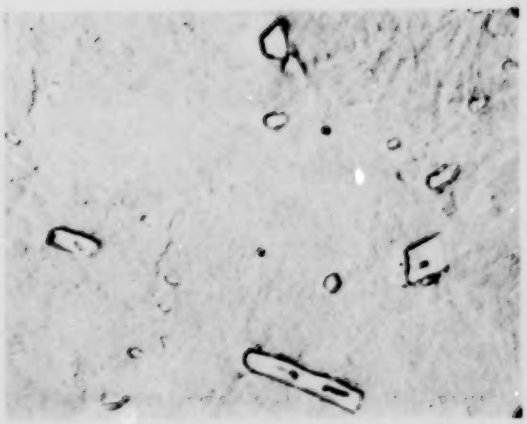
X-Ray Diffraction Analysis of Ti-2.5% Cerium Zirconate

2θ = 19.0°			2θ = 20.0°					
I	Kev	d Spacing	I	Kev	d Spacing	Titanium	Cerium Zirconate	Cerium Oxide
	8.1	CuKα (fluorescence)						
				9.9(1)			3.22(10)	
3	11.8	3.18	2	11.3	3.15		3.08(100)	3.12(100)
1	13.0	2.89	1	12.0	2.97			
3	13.72	2.74					2.67(80)	2.71(29)
7	14.65	2.56	10	14.1	2.53	2.577(30)		
							2.45	
							2.375	
0	16.65	2.255	100	15.9	2.24	2.244		
							2.186	
			10	17,7	2.01		2.054	
3	19.35	1.94	5	18.0	1.98		1.89(100)	1.91(50)
			1	19.6	1.82			
0	21.7	1.73	20	20.6	1.73	1.726		
								1.63
								1.56
0	25.35	1.48				1.475		



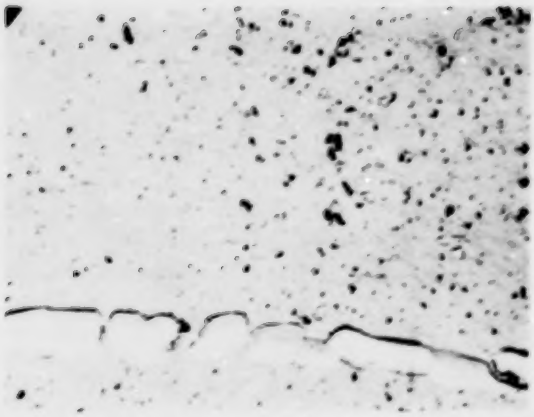
X5,000

Figure 1. Ti-1.5% ThO_2, arc melted.



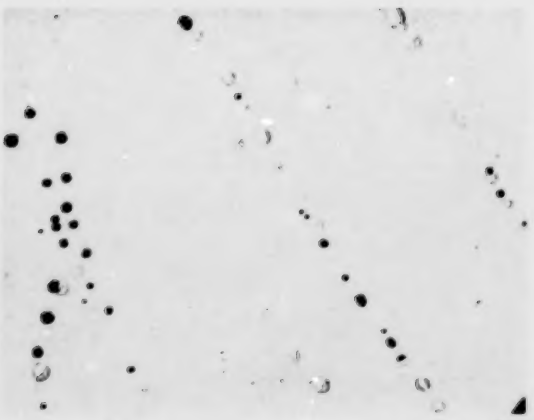
X5,000

Figure 2, Ti-2.5% ThO_2 , arc melted.



X5,000

Figure 3. Ti-5% ThO_2 , arc melted.



X5,000

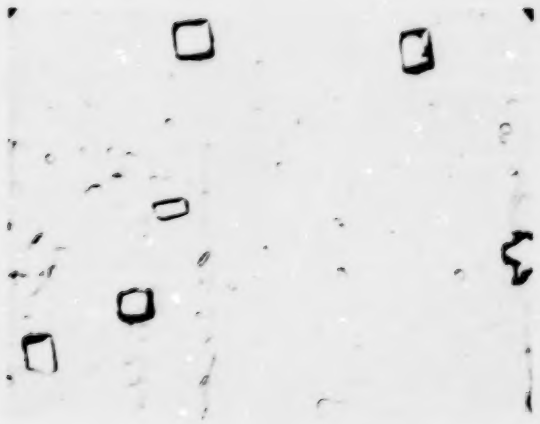
Figure 4. Ti-2.5% $Ce_2O_3.2ZrO_2$, arc melted.

X5,000

Figure 5. Ti-6%Al-4%V-5%ThO_2, annealed at 830°C for 2 hours, furnace cooled to 595°C then air cooled.

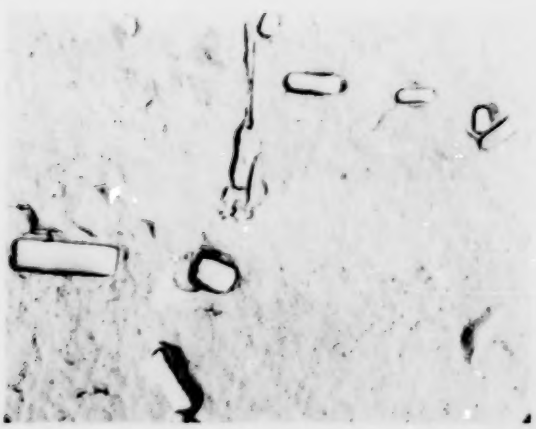
X5,000

Figure 6. Ti-6%Al-4%V-5%$Ce_2O_3 . 2ZrO_2$, annealed as in Figure 5.



X5,000

Figure 7. Ti-2.5%ThO_2, heat treated at 775°C 24 hours.



X5,000

Figure 8. Ti-2.5%ThO_2, heat treated at 950°C 24 hours.

X5,000

Figure 9. Ti-2.5%ThO_2, heat treated at 900°C 28 days.

X5,000

Figure 10. Ti-2.5%Ce_2O_3.2ZrO_2, heat treated at 950°C 24 hours.